

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C07F 15/02, C11D 3/39, B01J 31/18, C07B 33/00	A1	(11) International Publication Number: WO 97/48710 (43) International Publication Date: 24 December 1997 (24.12.97)
(21) International Application Number: PCT/US97/10764 (22) International Filing Date: 20 June 1997 (20.06.97) (30) Priority Data: 08/670,794 21 June 1996 (21.06.96) US (71) Applicant: REGENTS OF THE UNIVERSITY OF MINNESOTA [US/US]; 100 Church Street S.E., Minneapolis, MN 55455 (US). (72) Inventors: QUE, Lawrence, Jr.; 1084 Shryer Avenue West, Roseville, MN 55113 (US). KIM, Cheal; Apartment F, 1016 27th Avenue S.E., Minneapolis, MN 55414 (US). KIM, Jinheung; Apartment 89H, 1100 Highway 54 Bypass, Chapel Hill, NC 27516 (US). ZANG, Yan; Apartment 11, 1005 15th Avenue S.E., Minneapolis, MN 55414 (US). (74) Agent: RAASCH, Kevin, W.; Muetting, Raasch, Gebhardt & Schwappach, P.A., P.O. Box 581415, Minneapolis, MN 55458-1415 (US).		(81) Designated States: CA, JP, KR, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: IRON COMPLEXES FOR BLEACH ACTIVATION AND STEREOSPECIFIC OXIDATION (57) Abstract A bleach and oxidation catalyst is provided comprising a catalytically active iron complex which can activate hydrogen peroxide or peroxy acids, for example.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

**IRON COMPLEXES FOR BLEACH ACTIVATION
AND STEREOSPECIFIC OXIDATION**

Field of the Invention

5 The invention relates to iron complexes for use in bleach compositions, and for use in the stereospecific oxidation of organic substrates.

Background of the Invention

10 Peroxide bleaching agents for use in laundering have been known for many years. Such agents are effective in removing stains, such as tea, fruit, and wine stains, from clothing at or near boiling temperatures. The efficacy of peroxide bleaching agents drop off sharply, however, at temperatures below about 60°C. To lower the temperature at which peroxide bleaching agents are effective, metal complexes capable of activation of catalysis are combined with
15 the bleaching agents.

 For example, environmentally acceptable manganese ions and complexes are known for this purpose. U.S. Patent No. 4,728,455 discusses the use of a Mn(III)-gluconate complex as a peroxide bleach catalyst with high hydrolytic and oxidative stability. However, relatively high ratios of ligand
20 (gluconate) to Mn are needed to obtain the desired catalytic system. Moreover, the performance of this Mn-based catalyst is inadequate when used for bleaching in the low-temperature region of about 20-40°C. Furthermore, it is restricted in its efficacy at removing a wide range of stains. EP-A-458,379 discusses a triazacyclononane-based manganese complex that displays a high catalytic
25 oxidation activity at low temperatures, which is particularly suitable for bleaching purposes. It is believed that this improvement in bleaching activity is due to the fact that these compounds are stable under washing conditions, e.g., high alkalinity and oxidizing environment (as a result of the presence of hydrogen peroxide or peroxy acids).

30 In addition to the above-mentioned stain removal, dye transfer is a well-known problem in the art and has been addressed in various ways. For instance, an improved dye transfer inhibition has been obtained by using Fe-porphyrin and Fe-phthalocyanine complexes. See, for example, EP-A-537,381,

EP-A-553,607, EP-A-538,228.

It is well known that the stability of Fe-coordination complexes in alkaline aqueous media in the presence of peroxide compounds is very poor.

This poor stability of Fe-coordination species has resulted in the necessity of

5 very low concentrations of peroxide and, additionally, the use of polymers. See, for example, EP-A-538,228. These measures, however, only reduce the negative effects of this poor stability to some extent and do not provide a complete solution for the problem.

Improvement in activity and stability of iron compounds has been
10 recently disclosed in WO 95 34628. By employing pentadentate ligands, the stability of the iron species has been significantly enhanced. This resulted in a catalytic system that is particularly useful for stain removal and dye bleaching in solution. Still the synthesis of the complex, and in particular of the ligand employed, leaves room for improvement. Furthermore, the remarkable anti-dye
15 transfer properties have been obtained by using peroxyacids rather than hydrogen peroxide, which is desirable at least because of the expense associated with peroxyacids. Thus, there is a need for additional relatively stable complexes that can activate peroxy compounds in detergent compositions.

There is also a need for complexes that can stereospecifically
20 hydroxylate hydrocarbons. The stereospecific functionalization of aliphatic C-H bonds is important in chemistry and biochemistry for drug synthesis, perfume synthesis, etc. Such transformations have been carried out by organic peroxides in a stoichiometric fashion using oxidants such as (CF₃)₂-dioxirane, p-NO₂-perbenzoic acid, and perfluorodialkyloxaziridines, on substrates such as
25 1,2-dimethylcyclohexane and decalin. However, the prospect of using metal complexes in combination with readily available oxidants (e.g., O₂, H₂O₂, or ClO⁻) to carry out such reactions catalytically has aroused considerable interest in such endeavors. The latter has been inspired by the availability of metalloenzymes such as cytochrome P450, methane monooxygenase, and
30 dopamine β-hydroxylase, which respectively utilize a heme iron, a nonheme iron, and a copper center to catalyze stereospecific hydroxylation of an aliphatic C-H bond in an enzyme active site. Iron porphyrin complexes have been

successfully used as catalysts for stereospecific hydroxylation of hydrocarbons; however, the susceptibility of the porphyrin to oxidative self-degradation and the usual requirement for an expensive oxidant like PhIO have limited the utility of this approach.

5 There is also a need for complexes that can stereospecifically epoxidize hydrocarbons. Iron porphyrin and iron cyclam complexes have been used as catalysts for stereospecific epoxidation of C=C bonds; however, the catalysts were shown to be susceptible to oxidative self-destruction within a short period of time.

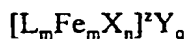
10

Summary of the Invention

The present invention provides a class of Fe-complexes that are surprisingly stable and active toward oxidation. Advantageously and preferably, these Fe-complexes display a high catalytic oxidation activity, particularly
15 stereospecific oxidation, when in the presence of a peroxy compound or precursor thereof. These complexes include tetradentate ligands and other ligands that are displaceable by the peroxy compound or precursor thereof. Significantly, preferred such complexes provide both favorable stain removal, remarkable dye transfer inhibition properties, and, alternatively, stereospecific
20 oxidation of organic substrates, particularly stereospecific hydroxylation and epoxidation.

One embodiment of the present invention is an Fe-complex, or precursor thereof, having the following formula (Formula A):

25



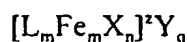
wherein:

- (a) Fe is iron in the II, III, IV, or V oxidation state;
- (b) X represents a coordinating species of the formula RCN, which is capable of coordinating to the Fe and being displaced by a peroxy
30 compound or precursor thereof, wherein R is an organic group;
- (c) L represents a tetradentate nontetraazamacrocyclic ligand, which is an organic molecule containing heteroatoms, capable of

coordinating to the Fe through all or some of its heteroatoms;

- (d) m is an integer ranging from 1 to 3;
- (e) n is an integer ranging from 0 to 7;
- (f) Y represents a counter ion, the type of which is dependent on the charge of the complex;
- (g) z denotes the charge of the complex and is an integer which can be positive, zero, or negative; and
- (h) $q = z/[\text{charge Y}]$.

A second embodiment is an Fe-complex, or precursor thereof, of the formula (Formula A):



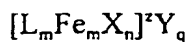
wherein:

- (a) Fe is iron in the II, III, IV, or V oxidation state;
- (b) X represents a coordinating species which is capable of coordinating to the Fe and being displaced by a peroxy compound or precursor thereof;
- (c) L represents a tetradentate nontetraazamacrocyclic ligand, which is an organic molecule containing heteroatoms, capable of coordinating to the Fe through all or some of its heteroatoms;
- (d) m is an integer ranging from 1 to 3;
- (e) n is an integer ranging from 0 to 7;
- (f) Y represents a counter ion, the type of which is dependent on the charge of the complex;
- (g) z denotes the charge of the complex and is an integer which can be positive, zero, or negative; and
- (h) $q = z/[\text{charge Y}]$.

Yet another embodiment is a detergent bleach composition prepared by combining components comprising:

- (a) an Fe-complex catalyst, or precursor thereof, of the formula

(Formula A):

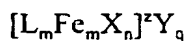


wherein:

- 5 (i) Fe is iron in the II, III, IV, or V oxidation state;
- (ii) X represents a coordinating species which is capable of coordinating to the Fe and being displaced by a peroxy compound or precursor thereof;
- 10 (iii) L represents a tetradentate nonporphyrin ligand, which is an organic molecule containing heteroatoms, capable of coordinating to the Fe through all or some of its heteroatoms;
- (iv) m is an integer ranging from 1 to 3;
- (v) n is an integer ranging from 0 to 7;
- 15 (vi) Y represents a counter ion, the type of which is dependent on the charge of the complex;
- (vii) z denotes the charge of the complex and is an integer which can be positive, zero, or negative; and
- (viii) $q = z/[\text{charge } Y]$;
- 20 (b) a peroxy bleaching compound, precursor thereof, or mixtures thereof;
- (c) a surface-active material; and
- (d) a detergency builder.

25 The present invention also provides methods for using the complexes of the present invention. One embodiment is a method of stereospecifically oxidizing an organic substrate comprising combining the substrate with a peroxy compound, precursor thereof, or mixtures thereof, with an oxidatively resistant Fe-complex catalyst, or precursor thereof, of the formula

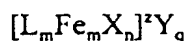
30 (Formula A):



wherein:

- (a) Fe is iron in the II, III, IV, or V oxidation state;
- (b) X represents a coordinating species which is capable of coordinating to the Fe and being displaced by a peroxy compound or precursor thereof;
- (c) L represents a tetradentate nontetraazamacrocyclic ligand, which is an organic molecule containing heteroatoms, capable of coordinating to the Fe through all or some of its heteroatoms;
- (d) m is an integer ranging from 1 to 3;
- (e) n is an integer ranging from 0 to 7;
- (f) Y represents a counter ion, the type of which is dependent on the charge of the complex;
- (g) z denotes the charge of the complex and is an integer which can be positive, zero, or negative; and
- (h) $q = z/[\text{charge Y}]$.

Another embodiment is a method of bleaching a substrate comprising contacting the substrate with a detergent bleach composition prepared by combining components comprising a peroxy compound, precursor thereof, or mixtures thereof, and an Fe-complex catalyst, or precursor thereof, of the formula (Formula A):



wherein:

- (a) Fe is iron in the II, III, IV, or V oxidation state;
- (b) X represents a coordinating species which is capable of coordinating to the Fe and being displaced by a peroxy compound or precursor thereof;
- (c) L represents a tetradentate nonporphyrin ligand, which is an organic molecule containing heteroatoms, capable of coordinating to the Fe through all or some of its heteroatoms;
- (d) m is an integer ranging from 1 to 3;

- (e) n is an integer ranging from 0 to 7;
- (f) Y represents a counter ion, the type of which is dependent on the charge of the complex;
- (g) z denotes the charge of the complex and is an integer which can
5 be positive, zero, or negative; and
- (h) $q = z/[\text{charge } Y]$.

The present invention also provides compositions prepared by combining a peroxy compound, precursor thereof, or mixtures thereof with an
10 Fe-complex of the present invention. As used herein, a peroxy compound is one that contains an O-O bond. A precursor of a peroxy compound is one that is capable of forming a peroxy compound. Thus, the term "peroxy compound precursor" includes dioxygen. A preferred group of peroxy compounds or precursors thereof include dioxygen, hydrogen peroxide, hydrogen peroxide -
15 liberating or -generating compounds, peroxyacids and their salts, peroxyacid precursors, and mixtures thereof.

As used herein, the term "organic group" means a hydrocarbon group that is classified as an aliphatic group, cyclic group, or combination of aliphatic and cyclic groups (e.g., alkaryl and aralkyl groups). In the context of
20 the present invention, the term "aliphatic group" means a saturated or unsaturated linear or branched hydrocarbon group. This term is used to encompass alkyl, alkenyl, and alkynyl groups, for example. The term "alkyl group" means a saturated linear or branched hydrocarbon group including, for example, methyl, ethyl, isopropyl, t-butyl, heptyl, dodecyl, octadecyl, amyl, 2-ethylhexyl, and the
25 like. The term "alkenyl group" means an unsaturated, linear or branched hydrocarbon group with one or more carbon-carbon double bonds, such as a vinyl group. The term "alkynyl group" means an unsaturated, linear or branched hydrocarbon group with one or more carbon-carbon triple bonds. The term "cyclic group" means a closed ring hydrocarbon group that is classified as an
30 alicyclic group, aromatic group, or heterocyclic group. The term "alicyclic group" means a cyclic hydrocarbon group having properties resembling those of aliphatic groups. The term "aromatic group" or aryl group" means a mono- or

polynuclear aromatic hydrocarbon group. The term "heterocyclic group" means a closed ring hydrocarbon in which one or more of the atoms in the ring is an element other than carbon (e.g., nitrogen, oxygen, sulfur, etc.).

As is well understood in this technical area, a large degree of substitution is not only tolerated, but is often advisable. Substitution is anticipated on the organic groups in the Fe-complexes of the present invention. As a means of simplifying the discussion and recitation of certain terminology used throughout this application, the terms "group" and "moiety" are used to differentiate between chemical species that allow for substitution or that may be substituted and those that do not allow or may not be so substituted. Thus, when the term "group" is used to describe a chemical substituent, the described chemical material includes the unsubstituted group and that group with O, N, or S atoms, for example, in the chain as well as carbonyl groups or other conventional substitution. Where the term "moiety" is used to describe a chemical compound or substituent, only an unsubstituted chemical material is intended to be included. For example, the phrase "alkyl group" is intended to include not only pure open chain saturated hydrocarbon alkyl substituents, such as methyl, ethyl, propyl, t-butyl, and the like, but also alkyl substituents bearing further substituents known in the art, such as hydroxy, alkoxy, alkylsulfonyl, halogen atoms, cyano, nitro, amino, carboxyl, etc. Thus, "alkyl group" includes ether groups, haloalkyls, nitroalkyls, carboxyalkyls, hydroxyalkyls, sulfoalkyls, etc. On the other hand, the phrase "alkyl moiety" is limited to the inclusion of only pure open chain saturated hydrocarbon alkyl substituents, such as methyl, ethyl, propyl, t-butyl, and the like.

Detailed Description of the Invention

Generally, the Fe-complexes of the invention may be used in compositions suitable for oxidation or bleaching comprising a peroxy compound, a precursor thereof, or mixtures thereof. The composition is suitable for use in the washing and bleaching of substrates including laundry, dishwashing and hard surface cleaning. Alternatively, the composition may be used in the textile,

pharmaceutical, flavor, fine chemical industries, paper and wood pulp industries, etc., for stereospecific oxidation processes, particularly stereospecific epoxidation or hydroxylation processes.

An advantage of the Fe-complexes according to the present invention is that they generally exhibit both a high oxidation activity and a remarkably high stability in alkaline aqueous media in the presence of peroxy compounds or precursors thereof.

They also generally exhibit a high oxidation activity and a remarkably high stability in the presence of peroxy compounds or precursors thereof during stereospecific oxidation, particularly hydroxylation of aliphatic C-H bonds and epoxidation of C=C bonds. Thus, in this context, the Fe-complex catalyst is oxidatively resistant. As used herein "oxidatively resistant" means that the Fe-complex catalyst remains active after the addition of at least about 25 equivalents of H_2O_2 at a rate of addition of 1 equivalent per minute at room temperature to an acetonitrile solution of an organic substrate. For hydroxylation, the substrate is cis-dimethylcyclohexane, and for epoxidation the substrate is cis-stilbene. In this context "active" means that the Fe-complex catalyst continues to hydroxylate or epoxidize the substrate. Preferably, the Fe-complex catalyst remains active after the addition of at least about 50 equivalents, and more preferably after the addition of at least about 100 equivalents, and even as high as several thousand equivalents, of H_2O_2 under the conditions specified above.

Another advantage of the Fe-complex catalysts of the invention is that their optimal bleaching activity is observed at lower pH values (e.g., at about 6-8 pH) than those observed for the triazacyclononane-based manganese complex compounds mentioned above. This advantage may turn out to be very beneficial in view of the current tendency to shift the pH during fabric washing from highly alkaline (typically, a pH of 10) to more neutral values.

An additional advantage is that such complexes are active as dye-transfer inhibition agents as shown in Example 3. A further advantage is that hydrogen peroxide can be employed to obtain effective dye bleaching in solution, rather than more expensive peroxyacids (although peroxyacids can also be used).

Another advantage is that the complexes of the invention have a relatively low molecular weight and are, consequently, very weight-effective. Furthermore, they can be easily prepared.

A further advantage is that the complexes of the invention give rise to stereospecific oxidation, as demonstrated by the stereospecific hydroxylation of aliphatic C-H bonds and stereospecific epoxidation of C=C bonds. Stereospecific oxidation entails the oxidation of an organic substrate, with retention of its stereochemistry. This type of reaction is important in a variety of processes in the flavor and pharmaceutical industries, for example. It is envisioned that the oxidation can also be enantiospecific with the appropriate choice of chiral ligand.

The Fe-complexes of the invention can be any iron co-ordination complex of the general Formula A:



wherein:

- (a) Fe is iron in the II, III, IV, or V oxidation state;
- (b) X represents a coordinating species which is capable of coordinating to the Fe and being displaced by a peroxy compound or precursor thereof;
- (c) L represents a tetradentate ligand, which is an organic molecule containing heteroatoms, capable of coordinating to the Fe through all or some of its heteroatoms;
- (d) m is an integer ranging from 1 to 3 (preferably m is 1 or 2);
- (e) n is an integer ranging from 0 to 7 (preferably n is 0 to 3);
- (f) Y represents a counter ion, the type of which is dependent on the charge of the complex;
- (g) z denotes the charge of the complex and is an integer which can be positive, zero, or negative; and
- (h) $q = z/[\text{charge } Y]$.

Precursors of the Fe-complex of Formula A are also suitable for

use in the present invention if they form the Fe-complex of Formula A under fabric washing conditions or oxidation conditions. Precursors typically include iron salts and the ligand L.

A preferred class of ligands is that of tetradentate ligands, which
5 coordinate via four heteroatoms, such as nitrogen, oxygen, and sulfur atoms, to the Fe atom. These heteroatoms are preferably nitrogen atoms or oxygen atoms, and more preferably nitrogen atoms. The nitrogen atoms can be part of tertiary, secondary, or primary amine groups, tertiary, secondary or primary amide groups, or part of heterocyclic aromatic ring systems, e.g., pyridines, pyrazines,
10 pyrazoles, imidazoles, benzimidazoles, thiazoles, triazoles, and pyrimidines, or combinations thereof. The oxygen atoms can be part of carboxylates, alcohols or phenols.

For certain preferred embodiments, L is a tetradentate nonporphyrin ligand. For other embodiments, L is a tetradentate
15 nontetraazamacrocyclic ligand. As used herein, a tetradentate nontetraazamacrocyclic ligand is a tetradentate ligand that does not contain four nitrogen atoms in a ring (such as are in porphyrin and phthalocyanine). Other macrocyclic ligands, such as those containing two or three nitrogen atoms in ring, for example, that are tetradentate are within the scope of this term.
20 Nonmacrocyclic ligands are also within the scope of this term. Furthermore, macrocyclic ligands with four heteroatoms other than nitrogen in the ring are also within the scope of this term.

Examples of suitable ligands in their unsubstituted forms are:
N,N,N-tris(pyridin-2-yl-methyl)amine; N,N,N-tris(pyrazol-1-yl-methyl)amine;
25 N,N,N-tris(imidazol-2-yl-methyl)methylamine; N,N,N-tris(benzimidazol-2-yl-methyl)methylamine; N,N,N-tris(1,2,4-triazol-1-yl-methyl)amine;
N,N,N-tris(2-amino-ethyl)amine; N,N,N-tris(2-(N,N-dimethyl)amino-ethyl)amine;
(N,N-bis(pyridin-2-yl-methyl)-amino)methylphenol; (N,N-bis(pyridin-2-yl-methyl)-amino)methylcarboxylic acid; (N,N-bis(pyridin-2-yl-methyl)-amino)ethanol; and
30 N,N'-bis(pyridin-2-yl-methyl)-ethylenediamine. Such ligands can also be

substituted as long as the substituents do not adversely affect bleaching and oxidation reactions. The most preferred ligand is N,N,N-tris(pyridin-2-yl-methyl)amine, hereafter referred to as TPA.

Ligand X is a coordinating species which is capable of
5 coordinating to the Fe and being displaced by a peroxy compound or precursor thereof. By this it is meant that, regardless of the mechanism and the actual coordinated ligand in the resultant active catalyst, ligand X is chosen such that it may be removed from the Fe center when combined with the peroxy compound or precursor thereof. Preferably, the coordinating species X is selected from the
10 group consisting of H_2O , ROH , NR_3 , RCN , OH^- , RS^- , RO^- , RCOO^- , OCN^- , SCN^- , N_3^- , CN^- , F^- , Cl^- , Br^- , I^- , O^{2-} , NO_3^- , NO_2^- , SO_4^{2-} , SO_3^{2-} , PO_4^{3-} , phenolates, alkoxalates or aromatic N donors such as pyridines, pyrazines, pyrazoles, imidazoles, benzimidazoles, pyrimidines, triazoles and thiazoles, and combinations thereof, wherein R is H or an organic group (preferably, an alkyl or cyclic organic group,
15 more preferably, having 1-100 carbon atoms, and most preferably $(\text{C}_1\text{-C}_6)$ alkyl moieties). More preferably, the coordinating species X is selected from the group consisting of OH^- , H_2O , RCN , O^{2-} , NO_3^- , SO_4^{2-} , aromatic N donors, and combinations thereof, wherein R is defined as above. Most preferably, X is selected from the group consisting of OH^- , H_2O , RCN , O^{2-} , and combinations
20 thereof, wherein R is defined as above.

Suitable counter ions are those which give rise to the formation of storage-stable solids. Combination of the preferred iron complexes with the counter ion Y preferably involves counter ions such as RCOO^- , BPh_4^- , ClO_4^- , BF_4^- , PF_6^- , RSO_3^- , SO_4^{2-} , NO_3^- , wherein R is H or an organic group. Preferably, R
25 is H, an alkyl or a cyclic organic group, more preferably having 1-100 carbon atoms, and most preferably $(\text{C}_1\text{-C}_6)$ alkyl moieties. If z is positive and Y is an anion selected from the group consisting of F^- , Cl^- , Br^- , I^- , NO_3^- , BPh_4^- , ClO_4^- , BF_4^- , PF_6^- , RSO_3^- , SO_4^{2-} , and CF_3SO_3^- , wherein R is an organic group.

The Fe-complexes of the present invention can be made from a
30 number of iron salts and tetradentate ligands. The complexes are typically prepared in the absence of oxygen by mixing equimolar amounts of iron salt and tetradentate ligand in CH_3CN or CH_3OH . for example, adding the X component

if necessary, and isolating the complex. The isolation of the complex may be accomplished by crystallization or precipitation by using a suitable counter ion Y or adding a suitable second solvent such as diethyl ether.

As previously stated, the Fe-complexes can be used to
5 sterespecifically oxidize organic substrates. The oxidation reactions are typically carried out in the absence of oxygen by mixing a degassed solution of organic substrates (e.g., cis-dimethyl-cyclohexane) in an organic solvent such as CH_3CN with the Fe-complex catalyst. To this solution is added a solution of peroxy compound or by slow addition, such as by a syringe pump at 30 $\mu\text{L}/\text{minute}$, at
10 room temperature.

The detergent bleach composition

The bleaching composition of the invention has particular application in detergent formulations to form a new and improved detergent
15 bleach compositions. Such detergent bleach compositions according to the present invention, include a peroxy compound or precursor thereof as defined above, the aforesaid Fe-complex catalyst having general formula (A), a surface-active material, and a detergency builder.

The Fe-complex catalyst will be present in the detergent bleach
20 composition of the invention in amounts so as to provide the required level in the wash liquor. Generally, the Fe-complex catalyst level in the detergent bleach composition corresponds to an iron content of from about 0.0005% to about 0.5% by weight. When the dosage of detergent bleach composition is relatively low, e.g., about 1-2 g/l, the Fe content in the formulation is suitably about
25 0.0025% to about 0.5%, preferably about 0.005% to about 0.25% by weight. At higher product dosages, as used, e.g., by European consumers, the Fe-content in the formulation is suitably about 0.00055% to about 0.1%, preferably about 0.001% to about 0.05% by weight. Higher levels may be desired and applied in industrial bleaching processes, such as textile and paper pulp bleaching. The
30 lower levels of the Fe-complex catalysts are preferably used in domestic laundry operations.

Detergent bleach compositions of the invention are effective over

a wide pH-range of between 6 and 13, with optimal pH-range lying between 7 and 11. This is particularly advantageous as the desire for detergent bleach compositions that are effective at neutral pH increases.

5 The peroxy compound

The peroxy bleaching compound, i.e., the peroxy compound and precursors thereof, may be a compound which is capable of yielding hydrogen peroxide in aqueous solution. Hydrogen peroxide sources are well known in the art. They include the alkali metal peroxides, organic peroxides such as urea
10 peroxide, and inorganic persalts, such as the alkali metal perborates, percarbonates, perphosphates persilicates and persulphates. Mixtures of two or more such compounds may also be suitable.

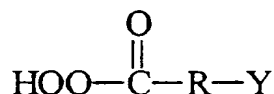
Particularly preferred are sodium perborate tetrahydrate and, especially, sodium perborate monohydrate. Sodium perborate monohydrate is
15 preferred because of its high active oxygen content. Sodium percarbonate may also be preferred for environmental reasons. The amount thereof in the composition of the invention usually will be within the range of about 5-35% by weight, preferably about 10-25% by weight.

Another suitable hydrogen peroxide generating system is a
20 combination of a (C₁-C₄)alkanol oxidase and a (C₁-C₄)alkanol, especially a combination of methanol oxidase (MOX) and ethanol (see Example 3). Such combinations are disclosed in International Application PCT/EP 94/03003 (Unilever), which is incorporated herein by reference.

Alkylhydroxy peroxides are another class of peroxy bleaching
25 compounds. Examples of these materials include cumene hydroperoxide and t-butyl hydroperoxide.

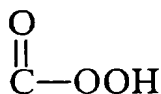
Organic peroxyacids may also be suitable as the peroxy bleaching compound. Such materials normally have the general formula:

30



wherein R is an alkylene or substituted alkylene group containing from 1 to about 20 carbon atoms, optionally having an internal amide linkage; or a phenylene or substituted phenylene group; and Y is hydrogen, halogen, alkyl, aryl, an imido-aromatic or non-aromatic group, a COOH or

5



group or a quaternary ammonium group.

Typical monoperoxy acids useful herein include, for example: peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g., peroxy- α -naphthoic acid; aliphatic, substituted aliphatic and arylalkyl monoperoxyacids, e.g., peroxy lauric acid, peroxy stearic acid and N,N-phthaloylaminoperoxy caproic acid (PAP); and 6-octylamino-6-oxo-peroxyhexanoic acid. Typical diperoxyacids useful herein include, for example: 1,12-diperoxydodecanedioic acid (DPDA); 1,9-diperoxyazelaic acid; diperoxybrassicic acid; diperoxysebacic acid and diperoxyisophthalic acid; 2-decyldiperoxybutane-1,4-dioic acid; and 4,4'-sulphonylbis(2,2,2-trifluoroethyl)peroxybenzoic acid.

Also inorganic peroxyacid compounds are suitable, such as for example, potassium monopersulphate (MPS). If organic or inorganic peroxyacids are used as the peroxygen compound, the amount thereof will normally be within the range of about 2-10% by weight, preferably about 4-8% by weight.

All these peroxy compounds may be utilized alone or in conjunction, particularly in combination with a peroxyacid bleach precursor, and/or in combination with an organic bleach catalyst not containing a transition metal.

Peroxyacid bleach precursors are known and amply described in literature, such as in the British Patents 836988; 864,798; 907,356; 1,003,310 and 1,519,351; German Patent 3,337,921; EP-A-0185522; EP-A-0174132; EP-A-0120591; and US Patents 1,246,339; 3,332,882; 4,128,494; 4,412,934 and 4,675,393.

Another useful class of peroxyacid bleach precursors is that of the cationic, i.e., quaternary ammonium substituted peroxyacid precursors as disclosed in US Patent 4,751,015 and 4,397,757, in EP-A0284292 and EP-A-331,229. Examples of peroxyacid bleach precursors of this class are: 2-(N,N,N-trimethyl ammonium) ethyl sodium-4-sulphonphenyl carbonate chloride - (SPCC); N-octyl,N,N-dimethyl-N₁₀-carbophenoxy decyl ammonium chloride - (ODC); 3-(N,N,N-trimethyl ammonium) propyl sodium-4-sulphophenyl carboxylate; and N,N,N-trimethyl ammonium toluyloxy benzene sulphonate.

A further special class of peroxyacid bleach precursors is formed by the cationic nitriles as disclosed in EP-A-303,520 and in European Patent Specification No.'s 458,396 and 464,880.

Any one of these peroxyacid bleach precursors can be used in the present invention, though some may be more preferred than others. Of the above classes of peroxyacid bleach precursors, the preferred classes are the esters, including acyl phenol sulphonates and acyl alkyl phenol sulphonates; the acyl-amides; and the quaternary ammonium substituted peroxyacid precursors including the cationic nitriles.

Examples of said preferred peroxyacid bleach precursors or activators are sodium-4-benzoyloxy benzene sulphonate (SBOBS); N,N,N'-tetraacetyl ethylene diamine (TAED); sodium-1-methyl-2-benzoyloxy benzene-4-sulphonate; sodium-4-methyl-3-benzoyloxy benzoate; SPCC; trimethyl ammonium toluyloxy-benzene sulphonate; sodium nonanoyloxybenzene sulphonate (SNOBS); sodium 3,5,5-trimethyl hexanoyl-oxybenzene sulphonate (STHOBS); and the substituted cationic nitriles.

Generally, the bleaching composition of the invention can be suitably formulated to contain from about 2% to about 35%, preferably from about 5% to about 25% by weight, of the peroxy compound or precursor thereof. Typically, if a peroxy compound precursor, particularly a peroxyacid precursor is used, it is used in an amount of up to about 12%, preferably about 2-10% by weight, of the composition.

As an alternative to the above described peroxy compounds, molecular oxygen may be used as the oxidant. Because dioxygen is capable of

producing a peroxy compound, it is referred to herein as a peroxy compound precursor.

The surface-active material

5 The detergent bleach composition according to the present invention generally contains a surface-active material in an amount of from 10 to 50% by weight. Said surface-active material may be naturally derived, such as soap, or a synthetic material selected from anionic, nonionic, amphoteric, zwitterionic, cationic actives and mixtures thereof. Many suitable surface-active
10 materials are commercially available and are fully described in the literature, for example in "Surface Active Agents and Detergents". Volumes I and II, by Schwartz, Perry and Berch.

 Typical synthetic anionic surface-active materials are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl
15 radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher aryl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and ammonium alkyl sulphates, especially those obtained by sulphating higher (C₈-C₁₈) alcohols produced, for example, from tallow or coconut oil; sodium and ammonium (C₉-
20 C₁₀) alkyl benzene sulphonates, particularly sodium linear secondary (C₁₀-C₁₅ alkyl benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ester of the higher alcohols derived from tallow or coconut oil fatty acid monoglyceride sulphates and sulphonates; sodium and ammonium salts of sulphuric acid esters of higher (C₉-C₁₉) fatty alcohol alkylene oxide, particularly
25 ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and ammonium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting (C₈-C₂₀) alpha-olefins with sodium bisulphite and those derived by reaction paraffins with SO₂ and C₁₂
30 and then hydrolysing with a base to produce a random sulphonate; sodium and ammonium (C₇-C₁₂) dialkyl sulphonates; and olefin sulphonates which term is used to describe material made by reacting olefins, particularly (C₁₀-C₂₀) alpha-

olefins, with SO_3 and then neutralising and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium (C_{10} - C_{15})alkylbenzene sulphonates and sodium (C_{16} - C_{18})alkyl ether sulphates.

Examples of suitable nonionic surface-active compounds which may be used, preferably together with the anionic surface-active compounds, include, in particular, the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C_6 - C_{22}) phenols, generally 5-25 EO, i.e. 5-25 units of ethylene oxides per molecule; and the condensation products of (C_8 - C_{18})aliphatic primary or secondary linear or branched alcohols with ethylene oxide, generally 2-30 EO. Other so-called nonionic surface-active materials include alkyl polyglycosides, sugar esters, long-chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulfoxides.

Amphoteric or zwitterionic surface-active compounds can also be used in the compositions of the invention but this is not normally desired owing to their relatively high cost. If any amphoteric or zwitterionic detergent compounds are used, it is generally in small amounts in compositions based on the much more commonly used synthetic anionic and nonionic actives.

As disclosed by EP-A-544,490, the performance of the hereinbefore described bleach catalyst, may be dependent upon the active detergent system and the builder system present in the detergent bleach composition of the invention.

The detergent bleach composition of the invention will preferably comprise from 1-15% by weight of anionic surfactant and from 10-40 % by weight of nonionic surfactant. In a further preferred embodiment the detergent active system is free from (C_{16} - C_{12})fatty acids soaps.

The detergency builder

The composition of the invention normally and preferably also contains a detergency builder in an amount of from about 5-80% by weight, preferably from about 10-60% by weight.

Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4)

mixtures thereof.

Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate; nitrilotriacetic acid and its water-soluble salts; the alkali metal salts of carboxymethyloxy succinic acid, ethylene diamine tetraacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, citric acid; and polyacetal carboxylates as disclosed in U.S. Patent Nos. 4,144,226 and 4,146,495.

Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives, e.g. zeolite A, zeolite B (also known as Zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P type as described in EP-A-0384070.

In particular, the compositions of the invention may contain any one of the organic and inorganic builder materials, though, for environmental reasons, phosphate builders are preferably omitted or only used in very small amounts.

Typical builders usable in the present invention are, for example, sodium carbonate, calcite/carbonate, the sodium salt of nitrilotriacetic acid, sodium citrate, carboxymethyloxy malonate, carboxymethyloxy succinate and the water-insoluble crystalline or amorphous aluminosilicate builder material, each of which can be used as the main builder, either alone or in admixture with minor amounts of other builders or polymers as co-builder.

It is preferred that the composition contains not more than 5% by weight of a carbonate builder, expressed as sodium carbonate, more preferable not more than 2.5% by weight to substantially nil, if the composition pH lies in the lower alkaline region of up to 10.

Other ingredients

Apart from the components already mentioned, the detergent bleach composition of the invention can contain any of the conventional

additives in amounts of which such materials are normally employed in fabric washing detergent compositions. Examples of these additives include buffers such as carbonates, lather boosters, such as alkanolamides, particularly the monoethanol amides derived from palmkernel fatty acids and coconut fatty acids; lather depressants, such as alkyl phosphates and silicones; anti-redeposition agents, such as sodium carboxymethyl cellulose and alkyl or substituted alkyl cellulose ethers; stabilizers, such as phosphonic acid derivatives (i.e., DEQUEST types); fabric softening agents; inorganic salts and alkaline buffering agents, such as sodium sulphate, sodium silicate etc.; and usually in very small amounts, fluorescent agents; perfumes; enzymes, such as proteases, cellulases, lipases, amylases and oxidases; germicides and colourants.

When using a hydrogen peroxide source, such as sodium perborate or sodium percarbonate, as the bleaching compound, it is preferred that the composition contains not more than 5% by weight of a carbonate buffer, expressed as sodium carbonate, more preferable not more than 2.5% by weight to substantially nil, if the composition pH lies in the lower alkaline region of up to 10.

Of the additives, transition metal sequestrants, such as EDTA and the phosphonic acid derivatives, e.g., ethylene diamine tetra-(methylene phosphonate) referred to as "EDTMP," are of special importance, as not only do they improve the stability of the catalyst/H₂O₂ system and sensitive ingredients, such as enzymes, fluorescent agents, perfumes and the like, but also improve the bleach performance, especially at the higher pH region of above 10, particularly at pH 10.5 and above.

The invention will now be further illustrated by way of the following non-limiting Examples.

Example 1

Preparation of [Fe(TPA)(CH₃CN)₂](ClO₄)₂ · 2 H₂O

TPA · 3HClO₄ was synthesized according to literature methods, as disclosed in G. Anderegg et al., Chim. Acta., 50, pp. 2330-2332 (1967) and B. G. Gafford et al., Inorg. Chem., 28, pp. 60-66 (1989). The synthesis of this Fe(II)

complex was carried out under Ar by Schlenk line techniques.

$[\text{Fe}(\text{TPA})(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$. Equal mole amounts of TPA (0.29 g) and

$\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.36 g) were dissolved in acetonitrile. Complex

$[\text{Fe}(\text{TPA})(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$ was obtained as powder by adding diethyl ether

- 5 to this clear solution. Recrystallization from CH_3CN /diethyl ether yields pure complex which gives satisfactory elemental analysis results. Yield: 0.58 g (92%).

In Examples 2, 3, and 4, the above-described complex

$[(\text{TPA})\text{Fe}(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$ is referred to as $\text{Fe}(\text{TPA})$.

Characterization: ^1H NMR spectrum (CD_3CN): 10.9 ppm

- 10 (pyridine;a); 8.5 and 8.4 ppm (pyridine; b); 7.3 ppm (pyridine; c); and 6.3 ppm (CH_2). UV-Vis (CH_3CN): 394 nm (ϵ : 7000); 360 (ϵ : 6500). Anal. Calcd for $\text{C}_{22}\text{H}_{24}\text{Cl}_2\text{FeN}_6\text{O}_8$: C, 43.13; H, 3.86; N, 13.40. Found: C, 42.87; H, 3.86; N, 12.91.

Example 2

- 15 The bleaching activity of the Fe-catalyst prepared according to Example 1 was demonstrated in the presence hydrogen peroxide on standard tea-stained (BC-1) cotton test cloths.

- The experiments were carried out at 40°C and at a pH of 7, 8.5 and 10 in a temperature-controlled glass beaker equipped with a magnetic stirrer. thermocouple and a pH electrode. Two pieces of test cloth were stirred for 60 minutes in 1 liter of a 8.6×10^{-3} mol/l hydrogen peroxide solution in millipore water, containing concentrations of the compounds as indicated in Table 1. After rinsing with demineralised water, the test cloths were dried for 7 minutes in a microwave oven. The reflectance (R_{460}^*) of the test cloths was measured on a Macbeth 1500/plus colour measuring system including UV-filter before and after treatment. The difference (ΔR_{460}^*) between both reflectance values thus obtained gives a measure of the bleaching performance, i.e. higher ΔR_{460}^* values correspond to an improved bleaching performance.
- 25
- 30

TABLE 1

	conc. (mol/l)	ΔR_{460}^* pH = 7	ΔR_{460}^* pH = 8.5	ΔR_{460}^* pH = 10
blank	2		2	5
Fe(NO ₃) ₃	5x10 ⁻⁶	2	2	6
5 Fe(TPA)	5x10 ⁻⁶	5	4	7

In Table 1, Fe(TPA) refers to the Fe-complex catalyst prepared according to Example 1. The blanks and Fe(NO₃)₃ experiments were used as control.

These measurements show that improved bleaching performance is obtained when Fe(TPA) is present in solution; especially around pH7-8.5.

Example 3

The dye oxidation activity of the Fe-catalyst prepared according to Example 1 was demonstrated in the presence of hydrogen peroxide on a dye known as acid red 88.

The experiments were carried out at ambient temperature at pH = 6 and 7 in a 1 cm cuvet in the presence of 8.6x10⁻³ mol/l hydrogen peroxide and 2x10⁻⁴ mol/l acid red 88. The absorbance at 500 nm (A_{500}), which is the maximum of the characteristic visible absorption of the dye in aqueous media, was measured at t = 0, t = 5, and t = 15 minutes. The ratio ($\Delta A_{500} = A_{500}(t = 5)/A_{500}(t = 0 \text{ min})$) of the absorbance at t = 5 minutes and t = 0 gives a measure of the dye-oxidation performance, i.e. an improved dye-oxidation performance results in reduced ΔA_{500} values after 5 minutes. The ratio ($\Delta A_{500} = A_{500}(t = 15)/A_{500}(t = 0 \text{ min})$) of the absorbance at t = 15 minutes and t = 0 gives a measure of the dye-oxidation performance, i.e. an improved dye-oxidation performance results in reduced ΔA_{500} values after 15 minutes. The systems without iron salt or Fe(TPA) compound do not exhibit dye oxidation under these conditions ($\Delta A_{500} = 1.00$). In all cases the concentration of catalyst is 5x10⁻⁶ M.

TABLE 3

	time	$\Delta A_{500}/\text{pH} = 6$	$\Delta A_{500}/\text{pH} = 7$
Fe(NO ₃) ₃	5 minutes	0.98	0.99
Fe(TPA)	5 minutes	0.67	0.82
5 Fe(NO ₃) ₃	15 minutes	0.98	0.99
Fe(TPA)	15 minutes	0.55	0.72

Fe(TPA) in Table 2 refers to the Fe-catalyst prepared according to Example 1. The experiments with Fe(NO₃)₃ were used as controls.

10 These measurements show that improved dye oxidation performance is obtained when Fe(TPA) is present in solution. This effect has even observed after 5 min, showing that the anti-dye transfer capabilities are quite fast.

15 Example 4

The organic substrate oxidation activity of the Fe catalyst, prepared according to Example 1, was demonstrated in the presence of hydrogen peroxide or t-BuOOH on a range of organic substrates.

20 A degassed solution of 700 mM substrate (2.7 mL) in acetonitrile was added to 1.4 mg Fe(TPA) catalyst under argon. To this solution was added 0.3 mL of 70 mM oxidant in acetonitrile by syringe pump over 15 minutes at room temperature. The reaction solution was stirred for an additional 5 minutes to ensure complete reaction. Dichlorobenzene was added at this point as an internal standard and the solution was passed through silica gel column to
25 remove the catalyst. The eluent was analysed by GC-MS. Results are listed in Table 4. The numbers indicated in Table 4 represent the turnovers (e.g., mol product per mol catalyst). In a blank experiment or in the presence of Fe(NO₃)₃, essentially no oxidation products could be detected.

30 These non-limiting examples presented in the table shows that this novel iron complex gives rise to catalyzed hydroxylation reactions and even stereospecific hydrocarbon hydroxylation reactions with hydrogen peroxide as

oxidant.

TABLE 4

oxidant	substrate	product	turnover number
H ₂ O ₂	cyclohexene	2-cyclohexen-1-ol	1.3
		2-cyclohexen-1-one	0.5
		cyclohexene epoxide	3
H ₂ O ₂	cyclohexane	cyclohexanol	3.6
		cyclohexanone	0.2
		cyclohexene	0.14
t-BuOOH	cyclohexane	cyclohexanol	4.5
		cyclohexanone	0.2
		cyclohexene	1.8
H ₂ O ₂	cis-1,2-dimethyl-cyclohexane	1,2-dimethyl-cyclohexene	0.14
		2,3-dimethyl-cyclohexane	0.12
		cis-1,2-dimethyl-cyclohexan-1-ol	3.6
		trans-1,2-dimethyl-cyclohexan-1-ol	0.0
		2,3-dimethyl-cyclohexan-1-ol and 3,4-dimethyl cyclohexan-1-ol	1.2
t-BuOOH	cis-1,2-dimethyl-cyclohexane	1,2-dimethyl-cyclohexene	3.2
		2,3-dimethyl-cyclohexene	0.9
		cis-1,2-dimethyl-cyclohexan-1-ol	0.6
		trans-1,2-dimethyl-cyclohexan-1-ol	0.4
		2,3-dimethyl-cyclohexan-1-ol and 3,4-dimethyl cyclohexan-1-ol	2.2

Example 5

The organic substrate oxidation activity of the Fe catalyst, prepared according to Example 1, was demonstrated in the presence of hydrogen peroxide on a range of organic substrates.

5 A degassed solution of 700 mM substrate (2.7 mL) in acetonitrile was added to 2.4 mg $[\text{Fe}_2(\text{TPA})_2(\text{O})(\text{H}_2\text{O})_2](\text{ClO}_4)_4$ catalyst under argon. To this solution was added 0.3 mL of 70 mM oxidant in acetonitrile by syringe pump over 15 minutes at room temperature. The reaction solution was stirred for an additional 5 minutes to ensure complete reaction. Dichlorobenzene was added at
10 this point as an internal standard and the solution was passed through silica gel column to remove the catalyst. The eluent was analyzed by GC-MS. Results are listed in Table 5. The numbers indicated in Table 5 represent the turnovers (eg mol product per mol catalyst). In a blank experiment or in absence of the catalyst $[\text{Fe}_2(\text{TPA})_2(\text{O})(\text{H}_2\text{O})_2](\text{ClO}_4)_4$, essentially no oxidation products could be
15 detected.

These non-limiting examples presented in the table shows that this novel iron complex gives rise to catalyzed hydroxylation reactions and even stereospecific hydrocarbon hydroxylation reactions with hydrogen peroxide as oxidant.

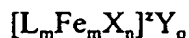
TABLE 5

oxidant	substrate	product	turnover number
H ₂ O ₂	cyclohexane	cyclohexanol	2.40
		cyclohexanone	0.85
		cyclohexene	0.12
	cyclooctane	cyclooctanol	2.40
		cyclooctanone	1.10
		cyclooctene	0.47
	cis-dimethyl-cyclohexane	1,2-dimethyl-cyclohexene	0.12
		2,3-dimethyl-cyclohexene	0.10
		cis-1,2-dimethyl-cyclohexan-1-ol	2.60
		trans-1,2-dimethyl-cyclohexan-1-ol	0.0
		2,3-dimethyl-cyclohexan-1-ol and 3,4-dimethyl-cyclohexan-1-ol	0.90
	trans-dimethyl-cyclohexane	1,2-dimethyl-cyclohexene	trace
		2,3-dimethyl-cyclohexene	0.13
		cis-1,2-dimethyl-cyclohexan-1-ol	0.0
		trans-1,2-dimethyl-cyclohexan-1-ol	0.90
		2,3-dimethyl-cyclohexan-1-ol and 3,4-dimethyl-cyclohexan-1-ol	1.3
	cis-stilbene	cis-stilbene oxide	1.2
		trans-stilbene oxide	trace
		benzaldehyde	0.7
		meso-hydrobenzoin	1.0

All patents, patent documents, and publications cited herein are incorporated by reference as if individually incorporated. The foregoing detailed description has been given for clarity of understanding only. No unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described, for variations obvious to one skilled in the art will be included within the invention defined by the claims.

WHAT IS CLAIMED IS:

1. An Fe-complex, or precursor thereof, having the following formula
(Formula A):



wherein:

- (a) Fe is iron in the II, III, IV, or V oxidation state;
 - (b) X represents a coordinating species of the formula RCN, which is capable of coordinating to the Fe and being displaced by a peroxy compound or precursor thereof, wherein R is an organic group;
 - (c) L represents a tetradentate nontetraazamacrocyclic ligand, which is an organic molecule containing heteroatoms, capable of coordinating to the Fe through all or some of its heteroatoms;
 - (d) m is an integer ranging from 1 to 3;
 - (e) n is an integer ranging from 0 to 7;
 - (f) Y represents a counter ion, the type of which is dependent on the charge of the complex;
 - (g) z denotes the charge of the complex and is an integer which can be positive, zero, or negative; and
 - (h) $q = z/[\text{charge } Y]$.
2. The Fe-complex of claim 1 wherein R is an alkyl group or a cyclic organic group.
 3. The Fe-complex of claim 2 wherein R is a (C₁-C₆) alkyl moiety.
 4. The Fe-complex of claim 1 wherein the heteroatoms of the tetradentate ligand are N, P, O, or S.
 5. The Fe-complex of claim 4 wherein the heteroatoms of the tetradentate ligand are nitrogen.

6. The Fe-complex of claim 4 wherein the tetradentate ligand is selected from the group consisting of N,N,N-tris(pyridin-2-yl-methyl)amine; N,N,N-tris(pyrazol-1-yl-methyl)amine; N,N,N-tris(imidazol-2-yl-methyl)methylamine; N,N,N-tris(benzimidazol-2-yl-methyl)methylamine; N,N,N-tris(1,2,4-triazol-1-yl-methyl)amine; N,N,N-tris(2-amino-ethyl)amine; N,N,N-tris(2-(N,N-dimethyl)amino-ethyl)amine; (N,N-bis(pyridin-2-yl-methyl)-amino)methylphenol; (N,N-bis(pyridin-2-yl-methyl)-amino)methylcarboxylic acid; (N,N-bis(pyridin-2-yl-methyl)-amino)ethanol; and N,N'-bis(pyridin-2-yl-methyl)-ethylenediamine.
7. The Fe-complex of claim 6 wherein the tetradentate ligand is N,N,N-tris(pyridin-2-yl-methyl)amine.
8. The Fe-complex of claim 7 wherein m is 1.
9. The Fe-complex of claim 1 wherein z is positive and Y is an anion selected from the group consisting of F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, BPh₄⁻, ClO₄⁻, BF₄⁻, PF₆⁻, RSO₃⁻, SO₄²⁻, and CF₃SO₃⁻, wherein R is an organic group.
10. An oxidatively resistant Fe-complex or precursor thereof, of the formula (Formula A):



wherein:

- (a) Fe is iron in the II, III, IV, or V oxidation state;
- (b) X represents a coordinating species which is capable of coordinating to the Fe and being displaced by a peroxy compound or precursor thereof;
- (c) L represents a tetradentate nontetraazamacrocyclic ligand, which is an organic molecule containing heteroatoms, capable of coordinating to the Fe through all or some of its heteroatoms;

- (d) m is an integer ranging from 1 to 3;
- (e) n is an integer ranging from 0 to 7;
- (f) Y represents a counter ion, the type of which is dependent on the charge of the complex;
- (g) z denotes the charge of the complex and is an integer which can be positive, zero, or negative; and
- (h) $q = z/[\text{charge } Y]$.

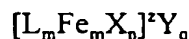
- 11. The Fe-complex of claim 10 which is oxidatively resistant.
- 12. The Fe-complex of claim 10 which is capable of stereospecifically oxidizing an organic substrate in the presence of a peroxy compound or precursor thereof.
- 13. The Fe-complex of claim 10 which is capable of enantiospecifically oxidizing an organic substrate.
- 14. The Fe-complex of claim 10 wherein the heteroatoms of the tetradentate ligand are N, P, O, or S.
- 15. The Fe-complex of claim 10 wherein the heteroatoms of the tetradentate ligand are nitrogen.
- 16. The Fe-complex of claim 10 wherein the tetradentate ligand is selected from the group consisting of N,N,N-tris(pyridin-2-yl-methyl)amine; N,N,N-tris(pyrazol-1-yl-methyl)amine; N,N,N-tris(imidazol-2-yl-methyl)methylamine; N,N,N-tris(benzimidazol-2-yl-methyl)methylamine; N,N,N-tris(1,2,4-triazol-1-yl-methyl)amine; N,N,N-tris(2-amino-ethyl)amine; N,N,N-tris(2-(N,N-dimethyl)amino-ethyl)amine; (N,N-bis(pyridin-2-yl-methyl)-amino)methylphenol; (N,N-bis(pyridin-2-yl-methyl)-amino)methylcarboxylic acid; (N,N-bis(pyridin-2-yl-methyl)-amino)ethanol; and N,N'-bis(pyridin-2-yl-methyl)-

ethylenediamine.

- 5
17. The Fe-complex of claim 16 wherein the tetradentate ligand is N,N,N-tris(pyridin-2-yl-methyl)amine and m is 1 or 2.
- 10
18. The Fe-complex of claim 10 wherein X is selected from the group consisting of H₂O, ROH, NR₃, RCN, OH⁻, RS⁻, RO⁻, RCOO⁻, OCN⁻, SCN⁻, N₃⁻, CN⁻, F⁻, Cl⁻, Br⁻, I⁻, O²⁻, NO₃⁻, NO₂⁻, SO₄²⁻, SO₃²⁻, PO₄³⁻, phenolates, alkolates, aromatic N donors, and combinations thereof, wherein R is H or an organic group.
- 15
19. The Fe-complex of claim 18 wherein X is selected from the group consisting of OH⁻, H₂O, RCN, O²⁻, and combinations thereof.
- 20
20. The Fe-complex of claim 10 which is capable of stereospecifically hydroxylating an aliphatic C-H bond.
21. The Fe-complex of claim 10 which is capable of stereospecifically epoxidizing a C=C bond.
- 25
22. A composition for oxidation prepared by combining components comprising the Fe-complex of claim 1 and a peroxy compound, precursor thereof, or mixtures thereof.
23. A composition for oxidation prepared by combining components comprising the Fe-complex of claim 10 and a peroxy compound, precursor thereof, or mixtures thereof.
- 30
24. The composition of claim 23 wherein the peroxy compound or precursor thereof is selected from the group consisting of dioxygen, hydrogen peroxide, hydrogen peroxide -liberating or -generating compounds, peroxyacids and their salts, peroxyacid precursors, and mixtures thereof.

25. A detergent bleach composition prepared by combining components comprising:

- (a) an Fe-complex catalyst, or precursor thereof, of the formula (Formula A):



wherein:

- (i) Fe is iron in the II, III, IV, or V oxidation state;
- (ii) X represents a coordinating species which is capable of coordinating to the Fe and being displaced by a peroxy compound or precursor thereof;
- (iii) L represents a tetradentate nonporphyrin ligand, which is an organic molecule containing heteroatoms, capable of coordinating to the Fe through all or some of its heteroatoms;
- (iv) m is an integer ranging from 1 to 3;
- (v) n is an integer ranging from 0 to 7;
- (vi) Y represents a counter ion, the type of which is dependent on the charge of the complex;
- (vii) z denotes the charge of the complex and is an integer which can be positive, zero, or negative; and
- (viii) $q = z/[\text{charge } Y]$;
- (b) a peroxy bleaching compound, precursor thereof, or mixtures thereof;
- (c) a surface-active material; and
- (d) a detergency builder.

26. The detergent bleach composition of claim 25 wherein the heteroatoms of the tetradentate ligand are N, P, O, or S.

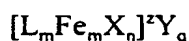
27. The detergent bleach composition of claim 26 wherein the heteroatoms of

the tetradentate ligand are nitrogen.

28. The detergent bleach composition of claim 25 wherein the tetradentate ligand is selected from the group consisting of N,N,N-tris(pyridin-2-yl-methyl)amine; N,N,N-tris(pyrazol-1-yl-methyl)amine; N,N,N-tris(imidazol-2-yl-methyl)methylamine; N,N,N-tris(benzimidazol-2-yl-methyl)methylamine; N,N,N-tris(1,2,4-triazol-1-yl-methyl)amine; N,N,N-tris(2-amino-ethyl)amine; N,N,N-tris(2-(N,N-dimethyl)amino-ethyl)amine; (N,N-bis(pyridin-2-yl-methyl)-amino)methylphenol; (N,N-bis(pyridin-2-yl-methyl)-amino)methylcarboxylic acid; (N,N-bis(pyridin-2-yl-methyl)-amino)ethanol; and N,N'-bis(pyridin-2-yl-methyl)-ethylenediamine.
29. The detergent bleach composition of claim 28 wherein the tetradentate ligand is N,N,N-tris(pyridin-2-yl-methyl)amine and m is 1 or 2.
30. The detergent bleach composition of claim 25 wherein X is selected from the group consisting of H_2O , ROH , NR_3 , RCN , OH^- , RS^- , RO^- , RCOO^- , OCN^- , SCN^- , N_3^- , CN^- , F^- , Cl^- , Br^- , I^- , O^{2-} , NO_3^- , NO_2^- , SO_4^{2-} , SO_3^{2-} , PO_4^{3-} , phenolates, alkylates, aromatic N donors, and combinations thereof, wherein R is H or an organic group.
31. The detergent bleach composition of claim 30 wherein X is selected from the group consisting of OH^- , H_2O , RCN , O^{2-} , and combinations thereof.
32. The detergent bleach composition of claim 25 comprising the peroxy compound, or precursor thereof, in an amount of from about 2% to about 35% by weight and the Fe-complex catalyst in an amount corresponding to an iron content of from about 0.0005% to about 0.5% by weight.
33. The detergent bleach composition of claim 25 comprising the surface-active material in an amount of from about 10% to about 50% by weight,

and the detergency builder in an amount of from about 5% to about 80% by weight.

34. The detergent bleach composition of claim 25 wherein the peroxy compound or precursor thereof is selected from the group consisting of dioxygen, hydrogen peroxide, hydrogen peroxide -liberating or -generating compounds, peroxyacids and their salts, peroxyacid precursors, and mixtures thereof.
35. A method of stereospecifically oxidizing an organic substrate comprising combining the substrate with a peroxy compound, precursor thereof, or mixtures thereof, with an oxidatively resistant Fe-complex catalyst, or precursor thereof, of the formula (Formula A):



wherein:

- (a) Fe is iron in the II, III, IV, or V oxidation state;
- (b) X represents a coordinating species which is capable of coordinating to the Fe and being displaced by a peroxy compound or precursor thereof;
- (c) L represents a tetradentate nontetraazamacrocyclic ligand, which is an organic molecule containing heteroatoms, capable of coordinating to the Fe through all or some of its heteroatoms;
- (d) m is an integer ranging from 1 to 3;
- (e) n is an integer ranging from 0 to 7;
- (f) Y represents a counter ion, the type of which is dependent on the charge of the complex;
- (g) z denotes the charge of the complex and is an integer which can be positive, zero, or negative; and
- (h) $q = z/[\text{charge } Y]$.

36. The method of claim 35 wherein the Fe-complex catalyst is capable of

stereospecifically hydroxylating an aliphatic C-H bond.

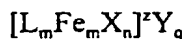
37. The method of claim 35 wherein the Fe-complex catalyst is capable of stereospecifically epoxidizing a C=C bond.

38. The method of claim 35 wherein the Fe-complex catalyst is capable of enantiospecifically oxidizing an organic substrate.

39. The method of claim 35 wherein:

- (a) X is selected from the group consisting of OH⁻, H₂O, RCN, O²⁻, and combinations thereof;
- (b) the tetradentate ligand is N,N,N-tris(pyridin-2-yl-methyl)amine;
- and
- (c) m is 1 or 2.

40. A method of bleaching a substrate comprising contacting the substrate with a detergent bleach composition prepared by comprising a peroxy compound precursor thereof, or mixtures thereof, and an Fe-complex catalyst, or precursor thereof, of the formula (Formula A):



wherein:

- (a) Fe is iron in the II, III, IV, or V oxidation state;
- (b) X represents a coordinating species which is capable of coordinating to the Fe and being displaced by a peroxy compound or precursor thereof;
- (c) L represents a tetradentate nonporphyrin ligand, which is an organic molecule containing heteroatoms, capable of coordinating to the Fe through all or some of its heteroatoms;
- (d) m is an integer ranging from 1 to 3;
- (e) n is an integer ranging from 0 to 7;
- (f) Y represents a counter ion, the type of which is dependent on the

charge of the complex;

- (g) z denotes the charge of the complex and is an integer which can be positive, zero, or negative; and
- (h) $q = z/[\text{charge } Y]$.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/10764

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07F15/02 C11D3/39 B01J31/18 C07B33/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07F C11D B01J C07B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	QUE L, JR. ET AL: "Modeling the oxygen activation chemistry of methane monooxygenase and ribonucleotide reductase" ACC. CHEM. RES. (ACHRE4,00014842);96; VOL.29 (4); PP.190-6, UNIVERSITY OF MINNESOTA;DEPARTMENT OF CHEMISTRY; MINNEAPOLIS; 55455; MN; USA (US), XP002040678 see the whole document and particularly page 196, left-hand column --- -/--	1-40

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *A* document member of the same patent family

Date of the actual completion of the international search

18 September 1997

Date of mailing of the international search report

30-09-1997

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Beslier, L

INTERNATIONAL SEARCH REPORT

International Application No

PC 1/US 97/10764

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DONG Y ET AL: "A High-Valent Nonheme Iron Intermediate. Structure and Properties of $[\text{Fe}2(\mu.-\text{O})2(5\text{-Me-TPA})2](\text{ClO}_4)_3$ " J. AM. CHEM. SOC. (JACSAT,00027863);95; VOL.117 (10); PP.2778-92, UNIVERSITY OF MINNESOTA;DEPARTMENT OF CHEMISTRY; MINNEAPOLIS; 55455; MN; USA (US), XP002040679 see the whole document ---	1-40
Y	WO 95 34628 A (UNILEVER N.V.) 21 December 1995 cited in the application see the whole document ---	1-40
Y	EP 0 392 592 A (UNILEVER N.V.) 17 October 1990 see the whole document ---	1-40
P,X	ZANG Y ET AL: "Models for Nonheme Iron Intermediates: Structural Basis for Tuning the Spin States of Fe(TPA) Complexes" J. AM. CHEM. SOC. (JACSAT,00027863);97; VOL.119 (18); PP.4197-4205, UNIVERSITY OF MINNESOTA;DEPARTMENT OF CHEMISTRY AND CENTER FOR METALS IN BIOCATALYSIS; MINNEAPOLIS; 55455; MN; USA (US), XP002040680 see the whole document -----	1-40

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/10764

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9534628 A	21-12-95	AU 2614895 A EP 0765381 A US 5580485 A	05-01-96 02-04-97 03-12-96
EP 392592 A	17-10-90	CA 2014321 A,C DE 69014384 D DE 69014384 T ES 2066099 T US 5114611 A	13-10-90 12-01-95 20-04-95 01-03-95 19-05-92